

Simple one-dimensional lattice model for lipids in water.

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Abstract

A lattice model for binary mixture of lipids and water is introduced and investigated. The orientational degrees of freedom of the amphiphilic molecules are taken into account in the same way as in the model for oil-water-surfactant mixtures introduced earlier by Johan Høye and co-authors. The ground state of the model is discussed in detail, and the mean-field stability analysis of the disordered phase is performed. The model is compared to the recently introduced lattice model for colloidal self-assembly.

I. INTRODUCTION

In 1987 Johan S. Høye, George Stell and Alina Ciach introduced a lattice model for ternary water, oil and surfactant mixtures (CHS model)[1]. The purpose of the highly simplified, generic model was a description of the universal properties of self-assembly in mixtures with amphiphilic molecules. Universality in this context means that the same properties can be found in many systems that differ by molecular details, but share the same property - namely the interaction between the amphiphilic molecules and the polar and nonpolar molecules depends significantly on the orientation of the former. Moreover, opposite orientations of the amphiphiles are favorable in the neighborhood of the polar and nonpolar particles, by which the presence of the oriented amphiphiles between water and oil is energetically favored. Elimination of unnecessary details allows for studies of the origin of such properties as the ultra-low surface tension and formation of lyotropic liquid crystals and bicontinuous microemulsion.

In the model introduced by Johan Høye and co-authors the orientational degrees of freedom of the water and oil molecules are disregarded, and their positions are discretized. In contrast, the orientational degrees of freedom of amphiphiles are taken into account, and both, the positional and the orientational degrees of freedom of the amphiphilic surfactant molecules are discretized. In a d -dimensional system $2d$ orientations of the amphiphiles are distinguished. Different orientations of the amphiphiles are treated as different components of the $2+2d$ component mixture, with equal values of the chemical potential associated with each component representing the amphiphilic molecules. Because of the distinguished orientations of the amphiphilic molecules, the significantly different interactions with the head and the tail of these molecules can be taken into account. However, the interaction between the oriented amphiphile at x and the water molecule at $x+1$ must be significantly different than the interaction between the same molecules, but with the water at x and the amphiphile in the same orientation at $x+1$.

Ground state of the model as well as the stability analysis and the phase diagram obtained in the mean-field (MF) approximation [2–4] reproduce the key properties of the oil-water-surfactant systems in the case of vanishing spontaneous curvature of the surfactant monolayer [5]. For weak surfactants coexistence of the oil- and water rich phases was obtained, whereas in the case of strong interactions between the water molecules and the

polar head of the surfactant, lamellar and bicontinuous microemulsion phases were found to be stable in certain conditions [2–4]. In addition, a cubic bicontinuous phase with diamond symmetry can be stable [6, 7]. The surface tension between the water and the periodic phase was found to be very low [4]. The origin of the low surface tension was attributed to the amphiphilic nature of the surfactant. When the highly unfavorable neighborhood of the water and oil molecules is replaced by the water-surfactant-oil sequence of molecules, then the energetically favourable pairs of the water and the head of the amphiphile and next the tail of the amphiphile and the oil lead to significant decrease of the energy. An interesting observation was that at the coexistence between the homogeneous and the periodic phases at $T = 0$ the ground state is strongly degenerated, and the surface tension vanishes [2]. The same property of the ground state was observed recently in a model with competing short-range attractive and long-range repulsive interactions [8]. Thus, it seems that the vanishing surface tension between coexisting uniform and periodic phases is not limited to the systems containing amphiphilic molecules. Later the CHS model was successfully used in studies of the effects of confinement on the self-assembling systems [5, 9–12].

Another, even more popular model for microemulsions is based on the phenomenological Landau-Brazovskii functional [13] of a single scalar order-parameter (OP). The functional has a form of a space integral with the integrand that consists of a polynomial in the OP ϕ , and in addition contains terms $u_2(\nabla\phi)^2$ and $u_4(\Delta\phi)^2$ with $u_2 < 0$ and $u_4 > 0$. The periodic ordering is favoured by the negative u_2 , and the length scale of inhomogeneities is set by the ratio u_4/u_2 . This model was first adopted to block copolymers by Leibler [14], and next to microemulsions by Gompper and Schick [15]. In the case of microemulsions the OP describes the local concentration difference between the polar and nonpolar components. However, the Landau-type functionals depend on a number of phenomenological parameters with no direct relation to measurable quantities. In addition, such functionals are not valid for strong ordering, and the formation of lyotropic liquid crystalline phases, where the concentration waves with large amplitude become stable, cannot be reliably described. Moreover, the ground states that can give valuable information on the energetically favourable ordering can be investigated in the lattice models much more easily than in the case of unrestricted positions and orientations of the molecules. Thus, the microscopic lattice models have many advantages.

Although the CHS model was designed for microemulsions, it could be considered as a

coarse-grained model for symmetrical block-copolymers too. In the mapping of the CHS model on the model for copolymers, the surfactant-occupied cell is mapped on the part of the copolymer containing the covalent bonding of the two types of the chain, A and B, whereas the water- and oil occupied cells represent the regions occupied by the A and B monomers respectively. Because of the oil-water symmetry of the CHS model, the A- and B-chain lengths in the copolymer version of the model must be the same. For this reason the interesting phenomena associated with the chain asymmetry cannot be studied in the original CHS model. Likewise, the binary aqueous solutions of amphiphilic molecules such as lipids could not be investigated. Only recently a continuous version of the CHS model for a binary system was introduced [16] in order to investigate lamellar phases in wedge geometry.

In the present work we try to fill this gap and introduce a 1d lattice model for water and amphiphilic molecules inspired by the CHS model. The general version of the model allows to study small surfactants, lipids and even block copolymers within the same framework. Another motivation for this study is the recently discovered close similarity between the self-assembly and the microsegregation observed in systems with competing interactions. In Ref.[17] it was shown that the microemulsions, block copolymers, and colloid particles interacting with competing short-range attraction and long-range repulsion can all be described by the same Landau-Brazovskii functional. The difference between these systems is reflected in different physical nature of the order parameter (OP). The Landau-type functionals can be appropriate only in the case of weak ordering, i.e. for high reduced temperature. The question of similarity between the amphiphilic and colloidal self-assembly in the case of strong order (at low T) remains open. We expect closer analogy between the assembly of the colloid particles into clusters of various shape and assembly of amphiphiles into micelles in the binary system than in the oil-water-surfactant mixture. The comparison between the predictions of the recently introduced model for colloidal self-assembly and the model inspired by the CHS model should allow for a comparative study of the low- T properties of amphiphilic and colloidal self-assembly. We introduce the model in sec.2, describe the ground state in sec.3 and perform the MF stability analysis in sec.4. We close with short summary in sec.5.

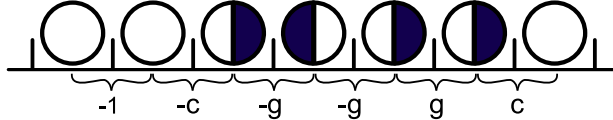


FIG. 1: The interacting pairs of occupied sites in the 1d model. The open circle represents the water molecule, and the light and dark semicircles represent the head and the tail of the lipid molecule respectively. The unit of the inscribed energies is the absolute value of the water-water interaction energy.

II. THE MODEL

We consider a two-component mixture of water and amphiphilic molecules, for example lipids. The amphiphilic molecules consist of a hydrophilic head and a hydrophobic tail, therefore the interactions between them depend on orientations. We assume that water molecules attract the hydrophilic head, and effectively repel the hydrophobic tail of the lipid molecule. In a one-dimensional model the continuum of different orientations of amphiphiles is reduced to just two orientations, one with the head on the left hand side and the other one with the head on the right hand side of the molecule. We neglect orientational degrees of freedom of the water molecules. In the case of charge-neutral lipids we assume nearest-neighbor interactions. The interactions are defined in a very similar way as in the lattice model for ternary oil-water-surfactant systems introduced by Høye, Stelltransactions and letters and one of the authors in 1987 [1–3]. The absolute value of energy of two water molecules that occupy the nearest-neighbour sites, $-b$, is taken as the energy unit. We assume that the interaction between the water molecule and the lipid molecule in the favourable (unfavourable) orientation is $-cb$ ($+cb$), and the interaction between two lipid molecules in the favourable and unfavourable orientation is $-gb$ and $+gb$ respectively. The orientations of two lipid molecules are favourable when they are oriented either head-to-head or tail-to-tail. The neighborhood of the polar head and the hydrophobic tail is unfavourable. The energies of different pairs of occupied sites are shown in Fig. 1.

We introduce the microscopic densities $\hat{\rho}_i(x)$ with $i = 1, 2, 3$ denoting water, lipid with the head on the left and lipid with the head on the right respectively. $\hat{\rho}_i(x) = 1$ when the site x is in the state i and $\hat{\rho}_i(x) = 0$ otherwise. Multiple occupancy of the lattice sites is excluded. The Hamiltonian of an open system, with the chemical-potential contribution

included, can be written in the form

$$\mathcal{H}[\{\hat{\rho}_i\}]/b = \frac{1}{2} \sum_x \sum_{x'} \hat{\rho}_i(x) V_{ij}(x, x') \hat{\rho}_j(x') - \sum_x \mu_i \hat{\rho}_i(x), \quad (1)$$

where the summation convention for repeated indices is used, $\mu_1 b$ is the chemical potential of water, and since the chemical potential of lipids, $\mu_s b$, is independent of orientations, $\mu_2 = \mu_3 = \mu_s$. According to the above discussion of interactions,

$$\mathbf{V}(x, x+1) = \begin{bmatrix} -1 & -c & c \\ c & g & -g \\ -c & -g & g \end{bmatrix} \quad (2)$$

and $V_{ij}(x, x-1) = V_{ji}(x, x+1)$.

We further restrict our attention to the liquid phase and assume close-packing. When each lattice site is occupied, then the microscopic densities satisfy the condition

$$\sum_{i=1}^3 \hat{\rho}_i(x) = 1. \quad (3)$$

We can eliminate $\hat{\rho}_1(x) = 1 - \hat{\rho}_2(x) - \hat{\rho}_3(x)$ in the energy contribution, and the Hamiltonian takes the form (up to a state-independent constant)

$$H[\{\hat{\rho}_i\}]/b = \frac{1}{2} \sum_x \sum_{x'} \hat{\rho}_i(x) U_{ij}(x, x') \hat{\rho}_j(x') - \sum_x \bar{\mu}_1 \hat{\rho}_1(x) \quad (4)$$

where $i, j = 2, 3$, $\bar{\mu}_1 = \mu_1 + 2 - \mu_s$ and

$$\mathbf{U}(x, x+1) = \begin{bmatrix} -1 + g & -1 - g - 2c \\ -1 - g + 2c & -1 + g \end{bmatrix}. \quad (5)$$

Again, $U_{ij}(x, x-1) = U_{ji}(x, x+1)$.

III. THE GROUND STATE

At $T = 0$ the stable structure corresponds to the global minimum of the Hamiltonian. The Hamiltonian in Eq.(4) for given interactions c and g takes the minimum for the densities $\hat{\rho}_i(x)$ that depend on $\bar{\mu}$. Apart from the water-rich and lipid-rich phases we expect stability of the periodic phase where lipid bilayers are separated by water layers. In the lipid-rich

phase the lipids are oriented head-to-head and tail-to-tail when $g > 0$. The values of H per lattice site, $h = H/L$, in these phases are

$$h/b = \begin{cases} -1 - \bar{\mu}_1 & \text{water} \\ -\frac{l-1+\bar{\mu}_1 l+2c+g(2n-1)}{l+2n} & \text{periodic} \\ -g & \text{lipid.} \end{cases} \quad (6)$$

In the periodic phase l water occupied sites are followed by $2n$ sites occupied by properly oriented lipid molecules. The coexistence lines obtained by equating h/b in these phases are

$$\bar{\mu}_1 = \begin{cases} g - 1 & \text{water-lipid} \\ \frac{2c+g-3}{2} & \text{water-periodic} \\ 2(g - c) & \text{periodic-lipid.} \end{cases} \quad (7)$$

The three phases coexist along the triple line $g = 2c - 1$ and $\bar{\mu}_1 = 2(c - 1)$.

Note that for the periodic phase we can write Eq.(6) in two equivalent forms,

$$h/b = \begin{cases} -(1 + \bar{\mu}_1) + \frac{2n(\bar{\mu}_1+1-g)+1-2c+g}{l+2n} \\ -g + \frac{l(g-1+\bar{\mu}_1)+g-2c+1}{l+2n}. \end{cases} \quad (8)$$

In the stability region of the periodic phase h/b in this phase is smaller than in the other two phases, therefore the second terms in both expressions in (8) must be negative. From the top line in (8) it follows that the lowest value of h/b is assumed for $l = 1$, and from the bottom line it follows that $n = 1$ in the stable structure. However, at the coexistence with the water phase the nominator in the second term in the top line in (8) vanishes. Since the periodic phase must be more stable than the pure lipid phase and therefore $n = 1$ (see the second line in (8)), we obtain that at the water-periodic phase coexistence the separation l between the lipid bilayers can be arbitrary. Thus, the ground state is strongly degenerated. Similar degeneracy occurs at the periodic-lipid phase coexistence. In this case $l = 1$ (the periodic phase is more stable than water). At the periodic-lipid coexistence the nominator in the second term in the bottom line in (8) vanishes, therefore the separation $2n$ between the water occupied sites is arbitrary.

Note that the arbitrary separation between the bilayers can be interpreted as the sponge or the disordered lamellar phase. On the other hand, the arbitrary separation between the bilayers is possible only at the coexistence between the water and the periodic phase, and can be interpreted as an arbitrary number of coexisting droplets of the two phases, which in

addition can have an arbitrary size. This in turn signals vanishing surface tension between the periodic and the water phases. Precisely the same properties, namely the coexisting droplets of the periodic and the lipid phases, and the associated vanishing surface tension, are found at the coexistence between the periodic and the lipid phases. It is interesting that in the 1d lattice model of particles interacting with the short-range attraction and long-range repulsion (SALR) potential the ground state has the same kind of degeneracy at the phase coexistence between the periodic and the gas or liquid phases [8]. Although the periodic phase in the case of colloidal self-assembly consists of periodically distributed clusters of particles which have neither shape nor interaction anisotropy, we obtain the same property of the ground state at the coexistence between the periodic phase and the other two phases.

Similar degeneracy of the ground state was found earlier for the lattice model of microemulsion [2]. The very low surface tension at the coexistence between the microemulsion and water rich phases was attributed to the amphiphilic nature of surfactant molecules. The results for the present model and for the model of colloidal self-assembly show that the low surface tension is a more general property of systems with competing interactions. When the ordered phases with spatial inhomogeneity coexist with each other or with homogeneous phases, the ground state is degenerated as discussed above. The degenerated ground state at the phase coexistence indicates vanishing surface tension between the coexisting phases.

The $(c, \bar{\mu}_1)$ ground state is shown in Fig. 2 for two fixed values of g , namely for $g = 0$ and for $g = c$. In each case the water-lipid coexistence occurs for small values of c ; $c \leq 1/2$ for $g = 0$ and $c \leq 1$ for $g = c$. Recall that c is the ratio between the energy of the pair of the water and the lipid transactions and letters molecules in the favourable orientation, and of two water molecules. When c is larger than at the triple point (tp), than the sequence of the stable phases for increasing $\bar{\mu}_1$ is: lipids - periodic - water. All three phases coexist at the tp, $c = 1/2$, $\bar{\mu}_1 = -1$ for $g = 0$ and $c = 1$, $\bar{\mu}_1 = 0$ for $g = c$. The ground states shown in Fig. 2 are very similar to the ground state in the 1d lattice model for the SALR potential [8]. This property confirms the observation of universality of the periodic ordering on the mesoscopic length scale that was derived under the assumption of weak ordering [17].

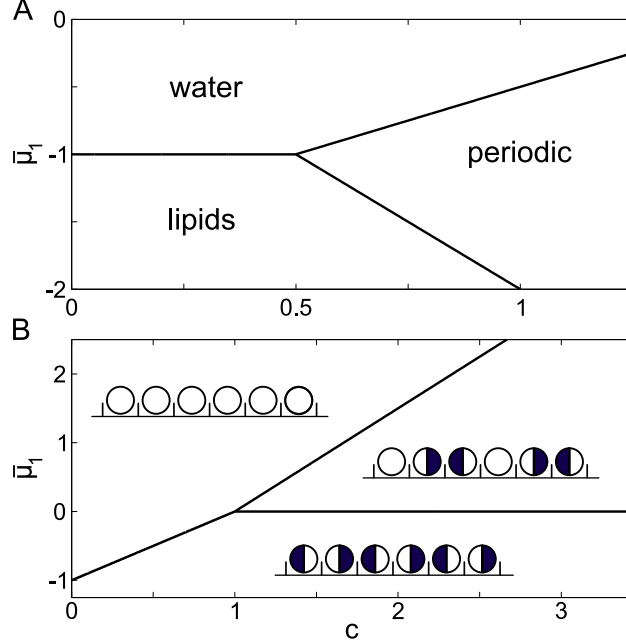


FIG. 2: The ground state of the model for $g = 0$ (panel A) and for $g = c$ (panel B). The triple point is at $(c, \bar{\mu}_1) = (0.5, -1)$ for $g = 0$ and $(1, 0)$ for $g = c$. On the B panel a schematic illustration of the three phases is shown in the insets inside the region of stability of each phase. The periodic phase is stable inside the indicated region for $l = 1$ and $n = 1$. At the coexistence with the water-rich phase the layers of water, l , can have an arbitrary length, and at the coexistence with the lipid phase the layers of lipids, $2n$, can have an arbitrary length.

IV. MEAN-FIELD STABILITY ANALYSIS

The grand thermodynamic potential in the mean-field (MF) approximation takes the form

$$\beta\Omega = \frac{1}{2} \sum_x \sum_{x'} \rho_i(x) \beta U_{ij}(x, x') \rho_j(x') - \mu^* \sum_x \rho_1(x) + \sum_x \sum_{n=1}^3 \rho_n(x) \ln \rho_n(x) \quad (9)$$

where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant, the indices in the first term are $i, j = 2, 3$ and summation convention is used for this term, $\rho_1(x) = 1 - \rho_2(x) - \rho_3(x)$, U_{ij} is defined in Eq.(5), $\mu^* = \beta \bar{\mu}_1$, and in thermal equilibrium the densities correspond to the minimum of Ω , i.e. $\delta\Omega/\delta\rho_i(x) = 0$ for $i = 2, 3$. The last term in (9) is the entropy contribution. In this section we shall determine the stability of the disordered phase with respect to concentration waves with the wavenumber $0 \leq k \leq \pi$. Macroscopic separation of water- and lipid-rich phases corresponds to $k = 0$. In the crystalline lipid phase the particles

are oriented head-to-head and tail-to-tail. This phase corresponds to the concentration wave with $k = \pi$, i.e. the period Φ is $2\pi/k = 2$. There are two sublattices in this phase. The sites of the first one are numbered with even x , and of the second one with odd x . $\rho_2(x) - \bar{\rho}_2 > 0$ for x belonging to one of the sublattices, whereas $\rho_3(x) - \bar{\rho}_3 > 0$ on the sites of the other sublattice, where $2\bar{\rho}_2 = 2\bar{\rho}_3 = \rho$ is the space-averaged density of lipids. For $0 < k < \pi$ the fluctuating bilayers of lipids oriented tail-to-tail are separated by layers of water. At the instability with respect to the k -mode

$$\det \tilde{\mathbf{C}}(k) = 0 \quad (10)$$

where

$$\tilde{C}_{ij}(k) = \frac{\delta^2 \beta \Omega}{\delta \tilde{\rho}_i(k) \delta \tilde{\rho}_j(-k)} \quad (11)$$

for $i, j = 2, 3$ and $\tilde{\rho}_i(k) = \sum_x \rho_i(x) \exp(ikx)$, with similar convention (tilde) for the Fourier transforms of the remaining functions. From (9) and (5) we obtain

$$\tilde{C}_{ij}(k) = \beta \tilde{U}_{ij}(k) + f_{ij} \quad (12)$$

where

$$\tilde{U}_{ii}(k) = 2\beta^*(g - 1) \cos k, \quad \tilde{U}_{23}(k) = \tilde{U}_{32}^*(k) = -2\beta^*[(1 + g) \cos k + 2ic \sin k] \quad (13)$$

and

$$f_{ij} = \left(\frac{2}{\rho} + \frac{1}{1 - \rho}\right) \delta_{ij}^{Kr} + \left(\frac{1}{1 - \rho}\right) (1 - \delta_{ij}^{Kr}). \quad (14)$$

From (10) we obtain the explicit expression for the reduced temperature T^* at the instability with respect to the density wave with the wavenumber k for given ρ

$$T^*(\rho, k) = -\rho \left[P \cos k \mp \sqrt{4c^2(1 - \rho) - Q \cos^2 k} \right] \quad (15)$$

where

$$P(g, \rho) = g - 1 + \rho \quad (16)$$

$$Q(c, g, \rho) = 4(1 - \rho)(c^2 - g) - P^2(g, \rho). \quad (17)$$

At the domain boundaries, i.e. for $\cos k = \pm 1$ we obtain

$$T^*(\rho, k) = \begin{cases} 2\rho(1 - \rho) & \text{for } k = 0 \\ 2g\rho & \text{for } k = \pi. \end{cases} \quad (18)$$

For given ρ the boundary of stability of the disordered phase corresponds to $T^*(\rho, k_b)$ such that $T^*(\rho, k)$ assumes a maximum for $k = k_b$. From the necessary condition $\partial T^*(\rho, k)/\partial k = 0$ we obtain

$$\cos^2 k_b = R, \quad R = \frac{c^2 P^2(g, \rho)}{(c^2 - g)Q(c, g, \rho)}. \quad (19)$$

The corresponding temperature is

$$T^*(\rho, k_b) = 4c\rho(1 - \rho)\sqrt{\frac{(c^2 - g)}{Q(c, g, \rho)}}. \quad (20)$$

The boundary of stability of the disordered phase for given density corresponds to $\max(T^*(\rho, 0), T^*(\rho, \pi), T^*(\rho, k_b))$. The instability with respect to $k_b \neq 0, \pi$ can occur provided that $0 \leq R \leq 1$. The R (see Eq.(19)) is a positive number less than 1 for $\rho \in (\rho_{min}, \rho_{max})$, where the boundaries depend on the strengths c, g of the interactions. For $1 > \rho > \rho_{max}$ and for $0 < \rho < \rho_{min}$ the instability with respect to the k_b mode does not occur. For $0 < \rho < \rho_{min}$ the instability of the disordered phase is given by $T^*(\rho, 0)$, and for $1 > \rho > \rho_{max}$ by $T^*(\rho, \pi)$. The boundaries of the interval (ρ_{min}, ρ_{max}) are found to be

$$\rho_{min} = \begin{cases} 1 - \frac{g^2}{2c^2 - g} & \text{if } c^2 < g < 2c^2 \\ 1 - 2c^2 + g & \text{if } g < c^2 \text{ or } g > 2c^2 \end{cases} \quad (21)$$

and

$$\rho_{max} = \begin{cases} 1 - 2c^2 + g & \text{if } c^2 < g < 2c^2 \\ 1 - \frac{g^2}{2c^2 - g} & \text{if } g < c^2 \text{ or } g > 2c^2. \end{cases} \quad (22)$$

We have found that $T^*(\rho, k_b) > T^*(\rho, 0), T^*(\rho, \pi)$ for $\rho_{min} < \rho < \rho_{max}$ and $0 < k_b < \pi$ when $c^2 > g$ and $2c^2 > g + g^2$.

The density interval (ρ_{min}, ρ_{max}) with the above properties does not exist for g, c located below the solid line in Fig. 3. For such parameters the instability is with respect to water-lipid phase separation or with respect to ordering of lipids into a stack of oppositely oriented bilayers.

Figs. 4A, 5A and 6A show the lines of instability for the parameters from different regions in Fig. 3, whereas Fig. 4B, 5B and 6B show corresponding periods of density oscillations.

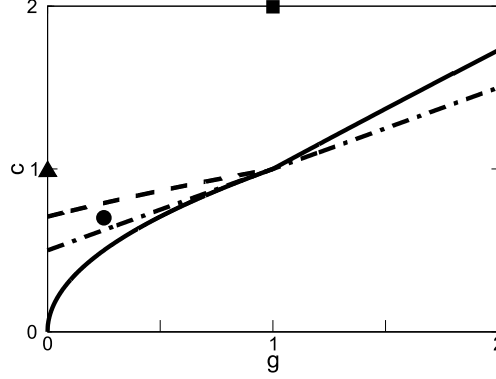


FIG. 3: The plane of the interaction parameters in units of the water-water interaction (see (2)) with indicated regions corresponding to different types of ordering. Above the solid line the disordered phase can become unstable with respect to oscillatory density with the period $\Phi = 2\pi/k_b \neq 2$ for some range of densities $\rho_{min} < \rho < \rho_{max}$ (formation of the amphiphilic bilayers). Above the dashed line the the instability with respect to periodic ordering occurs for $0 < \rho < \rho_{max}$. Below the dashed line the separation into water-rich and lipid phases occurs for $\rho < \rho_{min}$. The dash-dotted line is the projection of the three-phase line at $T = 0$ on the (c, g) plane. For the points marked by triangle $(1, 0)$, square $(2, 1)$ and circle $(c, g) = (0.7, 0.25)$ the MF instability lines and the period of density oscillations along the line $T^*(\rho, k_b)$ are presented at Figs. 4, 5 and 6 respectively.

V. DISCUSSION AND SUMMARY

We have developed a simple lattice model for water-lipid mixtures, inspired by the earlier lattice model for microemulsions introduced by Johan Høye and co-authors. Both the ground-state and the MF stability analysis show that the model predicts the key properties of aqueous solutions of amphiphilic molecules. It also helps to understand the relation between the low surface tension and the degeneracy of the ground state.

We have found strong similarity of the $T = 0$ phase diagrams of this model and the lattice model for colloidal self-assembly [8]. In the model introduced in Ref.[8] the nearest-neighbors attract each other, and the third neighbors repel each other. The repulsion results from screened electrostatic interactions of the charged particles. The phases with oscillatory density or concentration occur when the repulsion in the case of colloids or attraction between the water and properly oriented amphiphilic molecules in this model are strong. When the above interactions are weak, only two phases are present in the ground state - the gas and

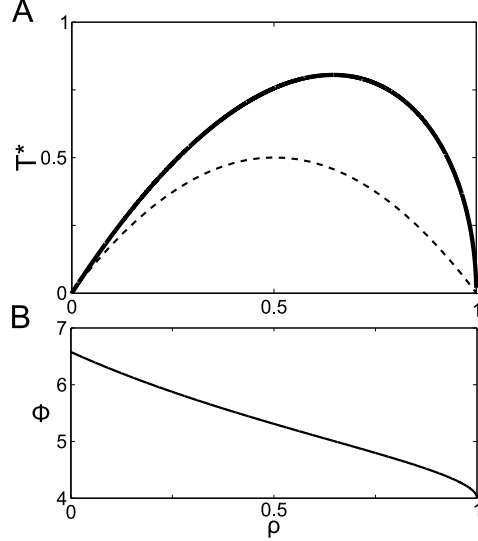


FIG. 4: Panel A: The $T^*(\rho, k_b)$ (solid), $T^*(\rho, 0)$ (short-dash) lines of MF instability with respect to formation of the lamellar phase (Eq.(20)) and water-lipid phase separation (Eq.(18)). The actual instability of the disordered phase is indicated by the thick line. Panel B: The period Φ of the density oscillations along the line of instability $T^*(\rho, k_b)$ as a function of the density of lipids. On both panels $(c, g) = (1, 0)$.

liquid in the SALR case and the water- and amphiphile rich phases in the present model. In both models the surface tension between the water and the periodic phase vanishes for $T = 0$, and the ground state is strongly degenerated. Arbitrary number of arbitrarily small droplets of the coexisting phases can be present at the phase coexistence. This degeneracy of the ground state means that the macroscopic separation of the two phases at $T = 0$ is not possible, since the formation of an interface does not lead to any increase of the grand potential. At the same time, because of the microscopic size of the droplets, one can interpret the degenerated ground state as a disordered phase. The region of the $T = 0$ phase diagram corresponding to the stability of this phase is of zero measure, however, in contrast to the remaining, ordinary phases. The properties of this phase resemble the microemulsion in the present model or a cluster fluid in the case of the model of colloids. Note that the inhomogeneous density, leading to the formation of the clusters, micelles or bilayers results from competing tendencies in the interactions, and not exclusively from the amphiphilic nature of the molecules.

The stability analysis shows that the main difference between the self-assembly in the

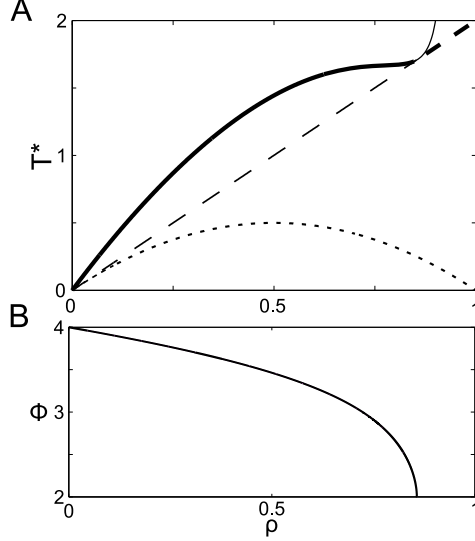


FIG. 5: Panel A: The $T^*(\rho, k_b)$ (solid), $T^*(\rho, \pi)$ (long-dashed) and $T^*(\rho, 0)$ (short-dash) lines of MF instability with respect to formation of the lamellar phase (Eq.(20)), crystallization of lipids, and water-lipid phase separation (Eq.(18)) respectively. The actual instability of the disordered phase is indicated by the thick line. Panel B: The period Φ of the density oscillations along the line of instability $T^*(\rho, k_b)$ as a function of the density of lipids. On both panels $(c, g)_{\text{transactions and letters}} = (2, 1)$.

amphiphilic and colloidal systems concerns the periodic ordering of the pure amphiphiles into the lamellar structure that is absent in the colloidal systems. Because of this crystal-like order of amphiphiles, the characteristic shape of the line of instability, similar to the spinodal line of the phase separation, is only found for $g = 0$, where the amphiphiles do not order in the absence of water. For $g > 0$ the shape of the line of instability in this model is similar to the corresponding line in the SALR system only for low volume fraction of amphiphiles. The interesting property of the model studied in Ref. [8], namely the phase separation for low T and periodic ordering for higher T is also found in this model for relatively weak interactions between water and amphiphiles.

To conclude, the present model for water-amphiphilic systems, based on the CHS model, demonstrates close similarity between different types of self-assembly. It also shows that there is still future for simple lattice models with complex phase behavior, such as the models recently investigated by Johan Høye and Enrique Lomba [18–20].

Acknowledgments This work is dedicated to Prof. Johan S. Høye. A part of this work

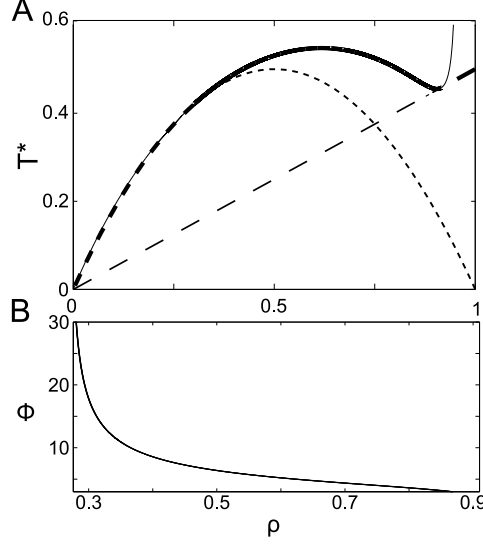


FIG. 6: Panel A: The $T^*(\rho, k_b)$ (solid), $T^*(\rho, \pi)$ (long-dashed) and $T^*(\rho, 0)$ (short-dash) lines of MF instability with respect to formation of the lamellar phase (Eq.(20)), crystallization of lipids, and water-lipid phase separation (Eq.(18)) respectively. The actual instability of the disordered phase is indicated by the thick line. Panel B: The period Φ of the density oscillations along the line of instability $T^*(\rho, k_b)$ as a function of the density of lipids. On both panels $(c, g) = (0.7, 0.25)$.

was realized within the International PhD Projects Programme of the Foundation for Polish Science, cofinanced from European Regional Development Fund within Innovative Economy Operational Programme "Grants for innovation".

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